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Native point defects in  $Y_3Al_5O_{12}$  (YAG) were studied in the framework of the pair-potential approximation coupled with the shell model description of the lattice ions. For the perfect lattice, a new set of potential parameters were obtained which reproduce structure, elastic and dielectric constants of YAG very well. The calculated formation energies for native point defects predict that the antisite disorder is preferred over the Frenkel and Schottky-like disorder in YAG. The calculated value of the distortion caused by the antisite  $Y_{Al}$  are in excellent agreement with the EXAFS measurements. In non-stoichiometric YAG, the calculated reaction energies indicate that excess  $Y_2O_3$  or  $Al_2O_3$  is likely to be accommodated by the formation of antisites rather than vacancies in the lattice.

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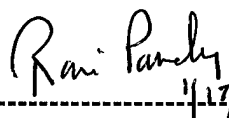
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## Executive Summary

This documentation is the final technical report for work performed under AFOSR grant F49620-96-1-0445 . The title of this project was "Atomistic calculations of defects in YAG" and the Principal Investigator was Ravi Pandey, Physics Department, Michigan Technological University, Houghton, MI 49931. This was 12-months research program to use atomistic modeling techniques to study defect energetics in YAG. During the grant's active period, the following report is submitted for publication :

- (i) Atomistic Modeling of Defects in YAG,  
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Native point defects in  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG) were studied in the framework of the pair-potential approximation coupled with the shell model description of the lattice ions. For the perfect lattice, a new set of potential parameters were obtained which reproduce structure, elastic and dielectric constants of YAG very well. The calculated formation energies for native point defects predict that the antisite disorder is preferred over the Frenkel and Schottky-like disorder in YAG. The calculated value of the distortion caused by the antisite  $\text{Y}_{\text{Al}}$  are in excellent agreement with the EXAFS measurements. In non-stoichiometric YAG, the calculated reaction energies indicate that excess  $\text{Y}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$  is likely to be accommodated by the formation of antisites rather than vacancies in the lattice.

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## I. INTRODUCTION

Yttrium aluminum garnet (YAG) is an important material whose technological applications range from lasers to propulsion systems. For example, the  $\text{Nd}^{3+}$  doped YAG is a well-known laser material whereas the  $\text{YAG:Al}_2\text{O}_3$  composite is found to be an ideal material for high-temperature structural ceramic applications.<sup>1</sup> Over the years, most of the experimental efforts have been focused on the understanding the optical<sup>2-6</sup> and magnetic<sup>7-10</sup> properties of dopant ions in the YAG lattice. However, relatively less attention has been paid to investigate its properties with an aim to exploit its potential in high-temperature applications.<sup>11-13</sup>

Diffusion and defect chemistry of pure and doped YAG have been a subject of a few experimental and theoretical studies.<sup>3,14-18</sup> An analysis of electroconductivity measurements and diffusion coefficients on a series of the crystals with the garnet structure has established that YAG is an ionic conductor. However, it has been suggested that the conductivity exhibits mixed ionic-electronic character.<sup>14</sup> for temperatures greater than 800°C. A similar conclusion was also achieved from the study of transport properties and defect formation of Ca- and Mg-doped YAG.<sup>16</sup>

A theoretical study based on the shell model has only considered the presence of vacancies and interstitials in the lattice predicting the dominance of vacancies over interstitials.<sup>17</sup> However, spectroscopic study of stoichiometry deviation in YAG has shown a possibility of cation antisite substitution in the garnet crystal lattice.<sup>19</sup> This has been confirmed very recently by the EXAFS measurements<sup>20</sup> in  $\text{Y}_2\text{O}_3$  rich YAG identifying the local order around the yttrium antisite atoms. Furthermore, the atomistic study of the defects in Yttrium Iron Garnet (YIG) by Donnerberg and Catlow<sup>21</sup> has also concluded that antisites, not vacancies, will dominate the intrinsic disorder in this material.

Due to a close similarity between YAG and YIG materials, it is therefore

expected that antisites are likely to play an important role in YAG and should be considered in any experimental or theoretical study of its defect chemistry.

In this paper, we seek to perform such a task reporting the results of a theoretical study of native defects in YAG. Our approach is based on the pair potential and shell model description of the ionic interactions in the crystalline lattice for which we will determine a new set of potential parameters. This set will then be used to study intrinsic disorder and reactions describing deviations from stoichiometry in YAG.

## II. METHOD

Partitioning of a crystalline lattice into two regions is the basis of the cluster model which is applied very often in calculations of defect properties in ionic materials. The main idea is to separate a cluster (referred to as region 1) from the rest of the lattice. It is also assumed that the perturbation caused by the defect in the crystal is weak beyond the cluster. The cluster is generally consisted of a limited region containing defect and several spheres of its nearest surroundings. A number of ions in the cluster varies from a problem to a problem and depends on the type of defects in the system. In calculations the cluster is treated explicitly within a selected method whereas the reminder of the lattice (represented by the region 2) is treated in an appropriate way. Thus, the crystal lattice energy can be written in the form:<sup>22</sup>

$$E = E_1(\vec{x}) + E_2(\vec{x}, \vec{\xi}) + E_3(\vec{\xi}), \quad (1)$$

where  $E$  is the total energy of the crystal,  $E_1(\vec{x})$  is the cluster energy,  $E_3(\vec{\xi})$  is the energy of the outer region,  $E_2(\vec{x}, \vec{\xi})$  is the energy of the interaction

between regions 1 and 2 depending from both ion coordinates of the cluster  $\vec{x}$  and the rest of the crystal  $\vec{\xi}$ . The exact expression for the crystal energy can be written as a series of interaction terms containing n-body components. The interionic potential model used in the present work is well described elsewhere, that is why we give here only main ideas and do not stop on the details. The method assumes that the total crystal energy can be given by a sum of all pairwise interactions in the lattice. In other words, all terms but two-body contribution are neglected in the series. Then one can write

$$E = \sum_{i>j} E(i, j), \quad (2)$$

where

$$E(i, j) = \phi_{ij}(r_{ij}) + q_i \cdot q_j / r_{ij}. \quad (3)$$

$E(i, j)$  is the energy of the interaction between ions  $i$  and  $j$ , with charges  $q_i$  and  $q_j$  located at the distance  $r_{ij}$ . The  $\phi_{ij}(r_{ij})$  is some suitable pair potential describing short-range interaction between ions. The latter is a result of atom repulsion due to their electron shell overlapping and dispersion attraction. For ionic materials this is generally chosen to take the form of a Buckingham potential:<sup>23</sup>

$$\phi_{ij}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6 \quad (4)$$

$A_{ij}$ ,  $\rho_{ij}$  and  $C_{ij}$  are empirical parameters, that are usually fitted to crystalline properties.

Displacements of ions in inner region 1 are obtained explicitly by minimization of the total energy. For outer region 2, displacements of ions are determined by the electric field due to the effective charge of the defect in the framework of Mott-Littleton approximation.<sup>24</sup> For cubic materials such as YAG, the ionic displacements are isotropic and are given by:<sup>25, 26</sup>

$$\delta \vec{x} = \frac{v_c}{4\pi} \cdot \frac{([G^{-1}] \cdot \vec{q})(1 - \epsilon^{-1})}{(\vec{q}^T \cdot G^{-1} \cdot \vec{q})} D^x \quad (5)$$



in which  $\delta\vec{x}$  is a vector of displacements in  $x, y$  or  $z$  directions,  $D^x$  is the corresponding electric displacement,  $\vec{G}$  is the second derivative of the non-Coulombic interaction matrix, and  $\epsilon$  is the trace of the dielectric constant tensor.

The interionic potential model is significantly improved if one takes into account the electronic polarization introduced by the charged defects in the lattice. This can be done by the shell model of Dick and Overhauser<sup>27</sup> describing valence electrons as a massless charged *shell*, that is coupled with *core* of the ion by isotropic elastic forces. All formulae are still valid if one rewrites them substituting shell and core charges and coordinates instead of rigid-ion ones. Both shell and core charges and coupling constants of a shell and a core of the given ion are the parameters of the theory and are generally empirically derived.

### III. RESULTS AND DISCUSSION

Experimental studies of garnets started long ago since the garnet structure was originally solved by Menzer.<sup>28,29</sup> However, there are only a few theoretical investigations focussing on defect chemistry in garnets.<sup>17,30,21,31</sup> The garnet structure belongs to the space group Ia3d ( $O_h^{10}$ ). The cations are all in special positions labeled as  $a, c, d$  with no positional degrees of freedom, while the oxygen atoms are placed in the general positions 96( $h$ ). Yttrium occupies dodecahedral 24( $c$ ) positions whereas there are two different sites for aluminum ions, namely octahedral 16( $a$ ) and tetrahedral 24( $d$ ) in the lattice (see, for example,<sup>32</sup>). This leads to the formula of  $Y_3Al_2Al_3O_{12}$  which is commonly written as  $Y_3Al_5O_{12}$ . The unit cell is large and consists of 8 formula units (160 atoms). For calculations, the oxygen positional pa-

parameters in the lattice were taken from neutron diffraction measurements by Prince<sup>33</sup> and are given by  $x=-0.029$ ,  $y=0.053$  and  $z=0.151$ . The X-ray diffraction study by Euler and Bruce<sup>34</sup> reports the cation-oxygen distances in YAG to be 1.94 Å and 1.76 Å for  $\text{Al}^{3+}(a)\text{-O}^{2-}$  and  $\text{Al}^{3+}(d)\text{-O}^{2-}$ , respectively. Following Geller,<sup>35</sup> the most accurate value of the lattice constant for the stoichiometric  $\text{Y}_3\text{Al}_5\text{O}_{12}$  is  $12.000\pm0.002$  Å. Several other experimental studies find the lattice constant to be slightly higher which may be due to the presence of excess yttrium in the lattice.<sup>35,36</sup>

## A. Interatomic Potentials

For interatomic potential model, formal ionic charges are assigned to the host-lattice ions, thereby considering them as  $\text{Y}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{O}^{2-}$  in YAG. The short-range interaction terms considered in the model describe cation-oxygen and oxygen-oxygen interactions. The short-range interactions between cations are ignored as they generally become very small for large separations which are 2.99 Å for  $d(\text{Y-Al}(d))$ ; 3.67 Å for  $d(\text{Y-Y})$  and  $d(\text{Al}(d)\text{-Al}(d))$  and 5.19 Å for  $\text{Al}(a)\text{-Al}(a)$  in YAG.

Note that the parameters for the  $\text{O}^{2-}\text{-O}^{2-}$ -interaction are assumed to be transferable among a series of oxides and are taken from the work of Catlow *et al.*<sup>22,37,38</sup> They were obtained from Hartree-Fock calculations of the interaction of two negative oxygen ions. Since the accurate representation of ionic polarization of a crystalline lattice is known to be very important for defect modeling, we have considered all of the constituent ions of YAG (i.e.  $\text{Y}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{O}^{2-}$ ) as polarizable ions in the lattice. Model parameters are then fitted to experimentally known YAG crystal properties such as the structure, elastic and dielectric constants and are given in Table 1. (For

details of the fitting procedure, we refer to the reference<sup>39</sup>). As it can be seen from Table 2, the model parameters reproduce the crystalline properties of YAG very well thus providing us a sound basis for extending the model to defect calculations.

Recently, Bush *et al.*<sup>40</sup> have obtained a consistent set of pair potentials empirically fitted specifically to the experimentally measured lattice properties of crystal oxides including YAG. This set is in addition to the potential set used earlier by Schuh *et al.*<sup>17</sup> which was fitted to  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  structure properties.<sup>22,41</sup> Although these two sets of interatomic potentials yield good agreement with the experimental values of the lattice structure and elastic constants of YAG, they do not yield the low- and high-frequency dielectric constants correctly. In fact the dielectric constants are overestimated by the first parameter set (16.2 and 4.0) and are underestimated by the second set (8.1 and 2.9) as compared to the experimental values of 11.0 and 3.5. This discrepancy may be due to the different description of cationic polarizability. Bush's set considers rigid Y and polarizable Al and, in contrast, Schuh's set contains rigid Al and polarizable Y. On the basis of ionic radii, Y ion is expected to be more polarizable than Al one. As it is shown from our calculations, an inclusion of both Y and Al polarizabilities into the model allows us to describe dielectric properties of YAG very well. We note here that the accurate representation of the dielectric constants by the shell model is essential in getting reliable defect energies in ionic materials such as oxides.

To further check the adequacy of the derived potential parameters, we examine the stability of the YAG lattice with respect to its component oxides:



The reaction enthalpies come out to be -2.4 eV and -1.6 eV, respectively, per

YAG formula unit indicating that YAG is indeed a stable compound. These values could be compared with the corresponding reaction enthalpies for YIG that are -1.6 eV and -2.9 eV, respectively.<sup>21</sup>

It is to be noted here that the structure properties of orthorhombic perovskite-like  $\text{YAlO}_3$  and the garnet  $\text{Y}_4\text{Al}_4\text{O}_{12}$  compound are well reproduced by our potential model. For example, the calculated lattice constants of  $\text{YAlO}_3$  ( $a=5.104 \text{ \AA}$ ,  $b=5.260 \text{ \AA}$ ,  $c=7.648 \text{ \AA}$ ) are in good agreement with the experimental data (5.179, 5.329, 7.370, respectively<sup>42,43</sup>). For the cubic  $\text{Y}_4\text{Al}_4\text{O}_{12}$  the calculated lattice constant of  $12.106 \text{ \AA}$  is only 0.9 % larger than experimental value of  $11.989 \text{ \AA}$ .<sup>44</sup>

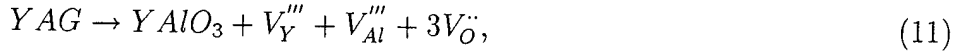
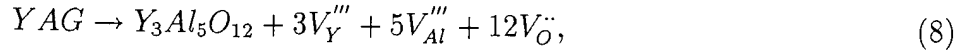
## B. Intrinsic Defect Structure

For calculations of native point defects in YAG, the lattice was simulated by a large cluster which contained more than 250 ions. The ions surrounding the defect in the cluster were allowed to relax until a minimum of the total energy was achieved. The rest of the lattice was considered in terms of Mott-Littleton approximation.<sup>24</sup> The calculations were performed using the GULP code.<sup>39</sup>

A vacancy formation was simulated as a removal of a regular lattice site ion to infinity. In order to model interstitials one ion was added to the crystal from infinity and was located in the empty interstitial position in the lattice. In the case of oxygen interstitials we probed all the possible positions in YAG which are referred to as  $f$  and  $g$ . For cations, the  $b$  positions were examined. The calculated formation energies for the isolated basic defects (which are collected in Appendix-Table A.2) can now be used to analyze the energetics of Schottky and Frenkel disorder in the lattice. For reader's convenience,

earlier potential sets<sup>17,40</sup> and the defect energies borrowed from<sup>17</sup> as well as obtained here using the corresponding set of pair potentials are given in Appendix for comparison.

Since YAG is a complex oxide and its lattice consists of three sublattices, the possible Schottky-like structure disorder can be written in the form:



where we use the notations of Kröger and Vink<sup>45</sup> for defects and the symbol "YAG" denotes the bulk crystal.

Here, the reaction (8) corresponds to the true Schottky disorder and remaining ones (9)-(11) are given as examples of a change in the chemical composition of the material. They can be interpreted as a possibility of self-segregation in stoichiometric YAG crystal by the Schottky-like disorder in either of the cation sublattices.

The Frenkel disorder can be written as



The computed formation energies (which are collected in Appendix-Table A.3) suggest that the Schottky-like disorder appears to be more favorable

than the Frenkel disorder. Nevertheless, even Schottky defect formation demands rather high energy (of about 3.9-4.7 eV per defect). Therefore, we can suppose that both Frenkel and Schottky defects are not likely to occur in YAG. This conclusion is in agreement with the results has been reported by Donnerberg and Catlow<sup>21</sup> for Yttrium Iron Garnet (YIG) crystals. Furthermore, large enthalpies of reactions (9)-(11) preclude the occurrence of self-segregation in stoichiometric YAG crystal as also observed experimentally.<sup>46</sup>

Next we consider antisite disorder in the cation sublattice of YAG which can be described as follows:



The corresponding antisite-pair formation energy is estimated to be about 0.9 eV and 1.8 eV per defect for the reactions (15) and (16), respectively, suggesting that the antisite disorder is preferred over Schottky and Frenkel disorder in YAG. We note here that Y prefers to be located at the Al(*a*) site over the Al(*d*) site. This is expected on the basis of the coordination numbers of these ions in the lattice: Y has coordination number of 8 whereas Al(*a*) and Al(*d*) ions have 6 and 4 near-neighbor oxygen ions, respectively (see Fig. 1). It is worth to note here that antisite pair formation in perovskite-like compound  $YAlO_3$  also demands very low energy which is 0.62 eV per defect indicating that these defects should play an important role in the material.

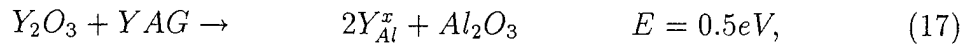
Experimental studies performed by Ashurov *et al.*<sup>19</sup> have in fact suggested that Y can occupy its regular dodecahedral sites as well as the Al(*a*) site in YAG. They investigated non-stoichiometric  $Y_3(Y_xAl_{2-x})Al_3O_{12}$  crystals by measuring the spectra of rare-earth impurity ions in the lattice and have concluded that the substitution of Y at the Al(*a*) site introduces the lattice distortion. Recent XANES and EXAFS measurements by Landron *et al.*<sup>20</sup>

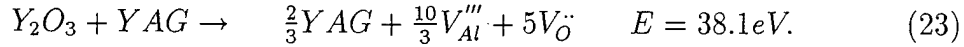
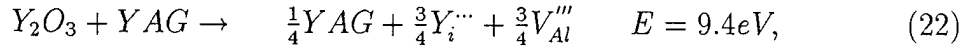
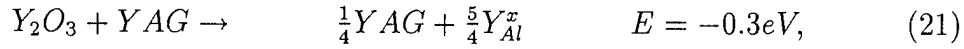
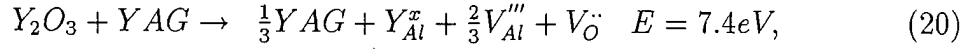
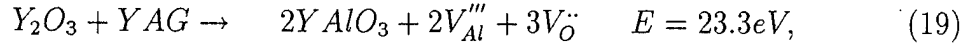
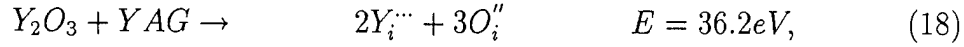
have investigated the local order around yttrium regular and antisite locations in  $Y_2O_3$  rich YAG. As it was shown, an increase of the electronegativity of the site ions after the substitution of Al cations by Y implies that the oxygen bond in the lattice becomes less ionic. The results in shortening of the distance between Y and O from  $d(Y-O)=2.43 \text{ \AA}$  to  $d(Y-O)=2.10 \text{ \AA}$  and is now close to the mean distance  $d(Y-O)$  of yttrium in octahedral position in yttria ( $Y_2O_3$ ). From our calculation, the substitution of Y at the Al(*a*) site in YAG lattice is accompanied by the decrease of the distance  $d(Y-O)$  to  $2.08 \text{ \AA}$  which is in excellent agreement with the experimental value of  $2.10 \text{ \AA}$ .<sup>20</sup>

### C. Deviations from Stoichiometry

Although experimental studies have long ago identified the presence of non-stoichiometric phases in YAG, the mechanism by which an excess of yttria or alumina can be accommodated in the lattice is not completely understood. In the early work on gallium and aluminum garnets,<sup>36</sup> excess of yttrium oxide was found to be soluble in the garnet. Geller<sup>35</sup> discussed a possible mechanism of the solid solution in the garnet structure which may involve vacancy or vacancy-interstitial complex instead of substitutional atoms. Neiman *et al.*<sup>14</sup> reported that the YAG structure can exist with some deficit of  $Al_2O_3$ . Several studies (see, for example,<sup>47,48</sup>) have also identified  $Al_2O_3$  inclusions in YAG ceramics. In this work, we make an aim to find the most probable mechanism of accommodating the deviations from stoichiometry in YAG structure.

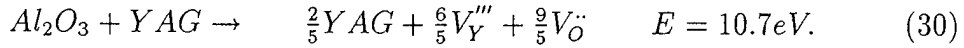
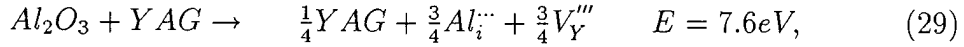
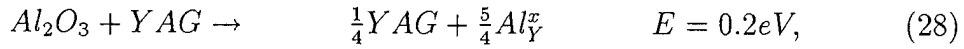
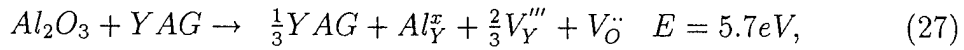
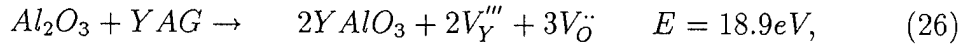
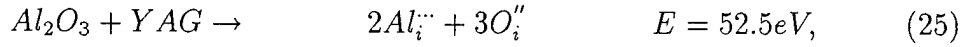
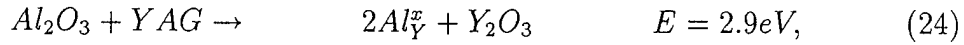
For  $Y_2O_3$  excess in YAG, we can write the following equations involving the formation of vacancies, interstitials and antisites:





The subscript Al refers to the regular  $Al_{(a)}$  lattice site in YAG and E is the calculated enthalpy of the given reaction.

Quite similarly we can describe the accommodation of excess of  $Al_2O_3$ :



Inspecting the list of the reactions and energies we notice that only reaction (21) has negative energy and is therefore exothermic. It leads to the conclusion that the antisite substitution of  $Y_{Al(a)}^x$  is the most favorable of all the possible mechanisms of accommodation of extra Y ions in YAG structure. This energy can be compared with the energy of the reaction (17) which describes antisite  $Y_{Al(a)}^x$  formation accompanied with segregation of  $Al_2O_3$  and shows a very small (endothermic) reaction enthalpy indicating a high probability of its occurrence. Alumina inclusion formations<sup>47,48</sup> may therefore be stimulated by yttria surplus in YAG. A deficit of alumina in the garnet structure, that was postulated by Neiman *et al.*,<sup>14</sup> indeed can exist



in YAG. Comparing the energies of reactions (21) and (28), we find that the  $Y_{Al(a)}^x$  antisite formation in  $Y_2O_3$  rich YAG is slightly more preferable over the formation of  $Al_Y^x$  in  $Al_2O_3$  rich YAG although the latter is still possible due to a small enthalpy of the process. Besides, these reactions indicate that extra Y ions can be accommodated in YAG lattice easier than Al ions. This fact is known from experiments. For example, an excess of  $Y_2O_3$  up to 2% was reported while an surplus of  $Al_2O_3$  in YAG was seen only up to 0.5% (see, for instance,<sup>18</sup>).

The formation of defect complexes like an interstitial and the corresponding vacancy (see reactions (22) and (29)) requires much more energy with respect to the antisite formation (reactions (21) and (28)). The required energy for the formation of interstitial defects described by reactions (18) and (25) are also very high as it was expected from Frenkel disorder energetics (see Section III.B). The segregation in the perovskite-like phase (reactions (19) and (26)) in YAG is also expected to have a low probability due to very high energy of the reaction.

The reaction (20) represents a mechanism of the defect accommodation predicted by Neiman *et al.* in<sup>14</sup> while equation (27) is composed by analogy. And the reactions (23) and (30) describe the process suggested by Sakaguchi *et al.* in.<sup>18</sup> From our calculations, both of these mechanisms are not predicted to take place in YAG crystal. The calculated results imply that the defect equilibrium in an excess material has different nature than that considered in these studies. Excess of neither of  $Y_2O_3$  nor  $Al_2O_3$  appears to be source of oxygen vacancies in pure YAG. It should be noted here, that an interaction between defects, that may be important under the conditions of large deviations from stoichiometry in materials, was not included in the present study.

## IV. CONCLUSIONS

In the present theoretical study, atomistic calculations of a formation of native point defects in Yttrium Aluminum Garnet crystal are performed. The Schottky and Frenkel defect formation energies are calculated as well as antisite substitutions in the cation sublattice. The calculated results show that:

1. intrinsic disorder in stoichiometric YAG is dominated by antisites;
2. antisite substitution  $Y_{Al(a)}^x$  causes a distortion in the crystalline lattice shortening the Y-O bond length whose calculated value is in excellent agreement with the EXAFS measurements;
3. excess of yttrium oxide  $Y_2O_3$  is energetically more favorable with respect to aluminum oxide  $Al_2O_3$  surplus in YAG;
4. formation of antisites in non-stoichiometric YAG is the most probable mechanism of accommodating the deviations from stoichiometry.

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TABLE 1. Interatomic potential parameters and shell constants. A,  $\rho$  and C are parameters in the equation for the Buckingham potential (see in the text, eq. (4));  $Y^+$  is charge of the core;  $K^+$  is core-shell spring constant.

Ion	A (eV)	$\rho$ (Å)	$Y^+$ ( $ e $ )	$K^+$ (eVÅ <sup>-2</sup> )	C (eVÅ <sup>-6</sup> )
O <sup>2-</sup> - O <sup>2-</sup> <sup>a)</sup>	22764.000	0.149	0.8481	74.92	27.88
Y <sup>3+</sup> - O <sup>2-</sup>	2036.8379	0.3103	-0.251	46.7288	0.0
Al <sup>3+</sup> - O <sup>2-</sup>	741.9007	0.3566	0.043	40.8618	0.0

<sup>a)</sup> potentials for O<sup>2-</sup> - O<sup>2-</sup> interaction are taken from G.V.Lewis and C.R.A.Catlow (Ref. 41).

TABLE II. Structural data for YAG calculated using interatomic potential parameter sets of:  
1. the present study; 2. Schuh *et al.*<sup>17</sup>; 3. Bush *et al.*<sup>40</sup>.

YAG	Cohesive energy (eV) per formula unit	Lattice parameters				Elastic constants (10 <sup>11</sup> dyn cm <sup>-2</sup> )			Relative permittivities	
		<i>a</i> (Å)	$\alpha^\circ$	<i>V</i> (Å)	$\rho$ (g/cm <sup>3</sup> )	<i>C</i> <sub>11</sub>	<i>C</i> <sub>12</sub>	<i>C</i> <sub>44</sub>	$\epsilon_0$	$\epsilon_\infty$
experiment	-	12.000 <sup>a)</sup>	90	867.45	4.53 <sup>b)</sup>	33.3 <sup>c)</sup>	11.3 <sup>c)</sup>	11.5 <sup>c)</sup>	11.0 <sup>d)</sup>	3.5 <sup>d)</sup>
present study	-589.28	11.988	90	861.36	4.58	34.0	12.7	11.2	11.4	3.5
Schuh <i>et al.</i>	-602.50	12.002	90	869.69	4.53	39.5	13.5	11.7	8.1	2.9
Bush <i>et al.</i>	-601.17	12.143	90	895.15	4.40	33.0	16.5	13.1	16.2	4.0

<sup>a)</sup> S.Geller<sup>35</sup>;

<sup>b)</sup> V.F.Kitaeva *et al.*<sup>2</sup>;

<sup>c)</sup> V.F.Kitaeva, E.V.Zharikov and I.L.Chisty, Phys. Stat. Sol. (a), 92, 475-88 (1985);

<sup>d)</sup> Landolt-Bornstein, Group III: Crystal and Solid State Physics in *Numerical Data and Functional Relationship in Science and Technology. New series*, ed. by K-H. Hellwege, volume 2, (Springer-Verlag, Berlin-Heidelberg-New-York, 1969).

## APPENDIX

Table A.1 shows the interionic potential and shell model parameter sets of Schuh *et al.*<sup>17</sup> and Bush *et al.*<sup>40</sup> Table A.2 gives basic isolated defect formation energies obtained using these parameter sets along with our derived set.

One of the most important advantages of the shell model is a correct description of optical modes of vibration, and as a result, a value of the high frequency dielectric constant. As it was shown (see sec. III.B), this value may be sensitive to the treatment of polarization of cations in the model.

Now we can analyze an influence of polarization on defect formation energy. Energies of Schottky-like and Frenkel disorder in YAG structure are collected in Table A.3 from which it is seen that the choice of potential does not change the main conclusion about preference of the disorder in YAG. However, a more careful look on the energetics of reactions reveals some sort of contradiction. The formation of Frenkel Y defects (reaction (13)) demands the highest energy using Schuh's set, whereas using parameters of Bush the highest energy comes out to be for Frenkel Al(d) defects (reaction (12)). The lowest energy among Frenkel pairs corresponds to Al (d) pair formation in the Schuh's set quite contrary to the Bush's results.

Furthermore, the probability of segregation of alumina and yttria (reactions (9) and (10)) is found to be comparable by Schuh's set. But Bush's set predicts a large difference between these reactions. Also, from Bush's parameters, segregation of yttrium oxide (reaction (10)) is only 0.4 eV less favorable than antisite pair formation in contrast to the Schuh's results.

These results lead to the conclusion that defect formation energy is very sensitive to the treatment of polarization effects in the lattice. Therefore, in order to get accurate results on energetics of the defect formation in YAG one should take carefully into account polarization of ions in the lattice.

TABLE A.I Interatomic potential parameters and shell constants of Schuh *et al.* <sup>17</sup> ;  
A,  $\rho$  and C are parameters in the equation for the Buckingham potential;  $Y^+$  is charge of the core;  $K^+$  is core-shell spring constant; C is attractive contribution.

Ion	A (eV)	$\rho$ (Å)	$Y^+$ ( $ e $ )	$K^+$ (eVÅ <sup>-2</sup> )	C (eVÅ <sup>-6</sup> )
O <sup>2-</sup> - O <sup>2-</sup>	22764.000	0.149	0.8481	74.92	27.88
Y <sup>3+</sup> - O <sup>2-</sup>	1345.1	0.3491	-0.251	71.70	0.0
Al <sup>3+</sup> - O <sup>2-</sup>	1469.3	0.2991	3.00	-	0.0

Interatomic potential parameters and shell constants of Bush *et al.* <sup>40</sup> .

Ion	A (eV)	$\rho$ (Å)	$Y^+$ ( $ e $ )	$K^+$ (eVÅ <sup>-2</sup> )	C (eVÅ <sup>-6</sup> )
O <sup>2-</sup> - O <sup>2-</sup>	25.41	0.6937	0.513	20.53	32.32
Y <sup>3+</sup> - O <sup>2-</sup>	1519.279	0.3291	3.00	-	0.0
Al <sup>3+</sup> - O <sup>2-</sup>	2409.505	0.2649	0.043	403.98	0.0

TABLE A.2. Intrinsic defects in YAG. Defect formation energies obtained using different parameter sets.

Vacancy formation energy (eV)				
Parameters set of	O	Y	Al (a-site)	Al (d-site)
present study	21.54	49.42	53.76	53.44
Schuh <i>et al.</i>	22.35 <sup>a)</sup>	46.5 <sup>a)</sup>	60.24 <sup>a)</sup>	58.9 <sup>a)</sup>
Bush <i>et al.</i>	17.63	47.74	59.94	65.10

Interstitial formation energy (eV)				
Parameters set of	O	O	Y	Al
	Symmetry position			
	g: (1/8, x, 1/4-x)	f: (x, 0, 1/4)	b: (1/8, 1/8, 1/8)	b: (1/8, 1/8, 1/8)
present study	-11.38	-11.79	-36.85	-40.72
Schuh <i>et al.</i>	-11.35	-11.06	-25.62 <sup>a)</sup>	-45.1 <sup>a)</sup>
Bush <i>et al.</i>	-8.33	-7.84	-33.51	-47.48

Antisite formation energy (eV)			
Parameters set of	Al in Y site	Y in Al(a) site	Y in Al(d) site
present study	-0.69	2.38	4.16
Schuh <i>et al.</i>	-10.45	13.53	14.29
Bush <i>et al.</i>	-8.93	11.52	12.78

<sup>a)</sup> from L.Schuh *et al.* <sup>17</sup>.



TABLE A.3. Reaction energies (per defect) in eV for Schottky-like, Frenkel and antisite disorder reactions obtained using different parameter sets. For details, see the text.

Reaction	Parameters set of		
	Present study	Schuh et al.	Bush et al.
Schottky-like			
(8)	4.26	5.32 <sup>a)</sup>	3.41
(9)	4.70	4.93	4.07
(10)	3.88	4.91	2.40
(11)	4.21	-	-
Frenkel			
(12): Al from (a) site	6.65	7.57 <sup>a)</sup>	6.23
(12): Al from (d) site	6.36	6.88 <sup>a)</sup>	8.81
(13): Y	6.28	10.44 <sup>a)</sup>	7.12
(14): O with (g) interstitial	5.08	5.50	4.65
(14): O with (f) interstitial	4.88	5.65	4.90
Antisite pair			
(15)	0.9	1.54	1.30
(16)	1.8	1.92	1.95

<sup>a)</sup> the value is taken from Schuh *et al.* <sup>17</sup>.

Figure caption for  
Atomistic modeling of defects in Yttrium Aluminum Garnet  
crystals  
by M.M.Kuklja and R.Pandey.

FIG. 1. Schematic representation of the arrangement of YAG in terms of the garnet structure. A fragment of a cluster is centered at: a). yttrium atom which is dodecahedrally coordinated (Y(c)); b). aluminum atom which is octahedrally coordinated (Al(a)); c). aluminum atom which is tetrahedrally coordinated (Al(d)) in the crystal.

Fig.

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